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ANALYSIS OF INNER AND OUTER SPHERE HYDROPHOBICITY EFFECTS IN
HETEROGENEOUS CATALYSIS USING SOLUTION THERMODYNAMICS

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ABSTRACT

Bio-oil produced via fast pyrolysis contains an appreciable quantity of water. Typical acid catalysts used to purify and stabilize bio-oil become solvated and are greatly inhibited by the presence of water. The development of a water tolerant acid catalyst would play an integral role in the effective stabilization of bio-oil and in the viability of bio-oil as an alternative fuel source. The proposed design of this study is to use a heterogeneous catalyst comprised of dispersed catalytic sulfonic acid active sites using high surface area mesoporous silica (SBA-15) as a support. The surface of the SBA-15 will be modified with organic functional groups in order to make the surface and local environment adjacent to the sulfonic acid moiety more hydrophobic. It is anticipated that the grafting of organic moieties on the surface of the SBA-15 will reduce solvation of the active site of the catalyst and in turn reduce inhibition by water that has been introduced upon formation of the bio-oil as a result of dehydration. Solution thermodynamics shows a strong correlation between the increasing hydrophobicity of inner-sphere and outer-sphere modifications on sulfonic acid catalysts and the decreasing solvation of the active site of the catalyst and the mesoporous silica support.

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Chapter 1

Introduction

Crude oil is in limited supply and is anticipated to run out within a few decades. Because of this, a push has been made to produce fuels from alternative sources. Bio-oil, a derivative of biomass, is one such possible alternative. Upgrading of bio-oil via chemical catalysis is essential in order for it to be converted to a viable fuel source. The catalysts currently used in the petroleum industry are not ideal for use in the conversion of biomass molecules due to the hydrophilic nature of biomass molecules as a result of their high oxygen content and their propensity to interact strongly with water. Many elementary biomass conversion reactions are catalyzed by acid catalysts, which can be strongly inhibited by the presence of water.¹ Therefore, it is necessary to design and/or modify heterogeneous catalysts in order to minimize solvation of the active site of the catalyst.

Biomass can be directly converted to bio-oil via fast pyrolysis.²⁻⁴ Bio-oil contains 10-30% water by weight and a number of small organic oxygenates (by weight: aldehydes- 10-20%, carboxylic acids-10-15%, phenols- 2-5%, furfurals- 1-4%, alcohols- 2-5%, ketones- 1-5%).³ The water content of bio-oil results from a combination of water formed during pyrolysis and the intrinsic moisture content of solid biomass.^{3,5} Due to its instability and corrosive nature, bio-oil must be upgraded before it can be used as a fuel source. The organic acids found in bio-oil catalyze oligomer forming reactions which convert bio-oil from its normally low-viscosity state to a high-viscosity fluid.⁶ It is therefore desired to eliminate residual organic acids from bio-oil. One such proposed solution for removing the organic acid content is esterification – reaction of the acid with an alcohol to yield an ester, as shown in Figure 1. Both reactants necessary for esterification– carboxylic acids and alcohols– are already present in bio-oil. Previous research by

Miao and Shanks¹ has found that water, also a product of esterification reactions, inhibits esterification at high conversion (high concentrations of water). Due to the already large fraction of water present in bio-oil, inhibition by water can be significant even at low conversion. An article from 2008 on using heterogeneous catalysis in the conversion of biomass from *Chemical and Engineering News* stated, “The biggest impediment to esterification of acids in bio-oil is the large concentration of water, which solvates the catalyst and shuts down its activity”.⁸

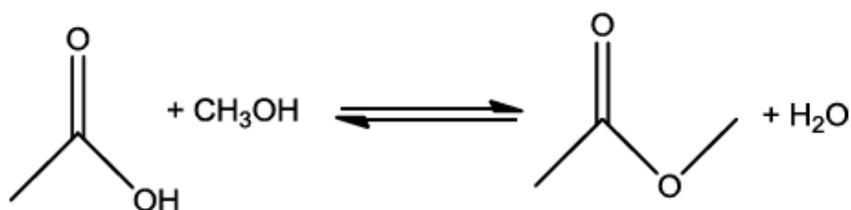


Figure 1. Model esterification reaction, acetic acid in methanol.

It is therefore desired to decrease solvation of the active site of the acid catalyst. Miao and Shanks' study on the effect of water on acid-catalyzed esterification reactions examined the apparent reaction orders of homogeneous acid catalysts, sulfuric acid (H_2SO_4) and propanesulfonic acid ($\text{CH}_3(\text{CH}_2)_2\text{SO}_3\text{H}$), in dioxane solution with varying amounts of water. It was found that the effect of water inhibition were significantly less for the reaction catalyzed by propanesulfonic acid.¹ The organic moiety (propyl side chain) appears to have an effect on proton solvation. Such effects will be referred to as inner-sphere effects throughout this study. Thermodynamic data available for sulfuric acid give the aqueous heat of solvation (heat of hydration) as ~ 23 kcal/mol, illustrating its very exothermic nature.⁷ No solution thermodynamic data was previously available for propanesulfonic acid. It is anticipated that the heat of solvation for propanesulfonic acid, and other sulfonic acids with larger organic moieties will be much less than that measured for sulfuric acid. It is further anticipated the heats of solvation for sulfonic acids with larger organic moieties (increased length of organic side chain) will be less than that

for sulfonic acids with smaller organic moieties. This is anticipated due to the increasing hydrophobic surface area of longer organic side chains. This study investigates the solution thermodynamics of various sulfonic acids in water and dioxane in an attempt to observe and explain these trends. It is expected that a correlation exists between the length of the side chain and the pKa of the acid. The pKa value is based on the dissociation of the acid proton in water. This study will examine the relationship between the pKa value of the acid and the solution thermodynamics of that acid in water.

Miao and Shanks and also examined heterogeneous sulfonic acid catalysts grafted on mesoporous silica. These catalysts were found to be less tolerant of water than their homogeneous analogs. It is suggested that the hydroxyl groups that accumulate on the silica surface are the primary cause for this increased sensitivity.¹ Modification of the organic moiety attached to the mesoporous silica support is a modification of the inner-sphere catalytic effect. It is anticipated that solvation of the active site of the catalyst will decrease as the size of the hydrophobic organic moiety increases. This study explores the inner-sphere effect of increasing hydrophobicity of the organic backbone of the acid catalysts through analysis of the heats of solution of the various homogeneous sulfonic acid catalysts. This study provides a basis for, but does not explicitly investigate these analogous effects on heterogeneous sulfonic acid catalysts. Figure 2 represents the inner-sphere effects.

Inner-sphere

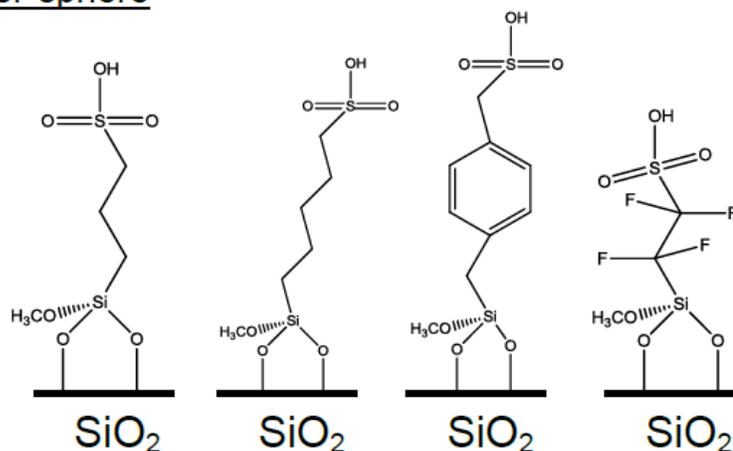


Figure 2. Inner-sphere effects - catalyst bound to mesoporous silica.

In order to further reduce solvation of the heterogeneous sulfonic acid catalysts, more hydrophobic modifications can be made to the mesoporous silica surface. Various silane grafting agents will be used to modify the outer-sphere hydrophobicity of the catalyst. Solution calorimetry will be used to measure the heats of wetting of the silane-grafted silicas. It is expected that the silane grafting agents with the most hydrophobic side chains will yield the most hydrophobic grafted silica. Figure 3 illustrates the hydrophobic cavity (highlighted in blue) created by the silane grafting modifications. This work will also investigate the effectiveness of silane grafting under different conditions. Two types of precursors will be used – alkoxy silanes and chlorosilanes. These will be evaluated to determine the best precursor for effective grafting. The silane grafting agents will be added in varying degrees of excess (based on the predetermined hydroxyl group density of the mesoporous silica) to further determine the most effective procedure for silane grafting.

Chapter 2

Experimental Section

Mesoporous silica, SBA-15, was synthesized following protocol reported by Zhao et al.⁹ Synthesized SBA-15 was dried under vacuum at 400°C for 4 hours. Three different alkoxy silanes— triethoxyphenylsilane, triethoxyoctylsilane, and trimethoxyoctadecylsilane- and six different chlorosilanes – chlorotrimethylsilane, trichloromethylsilane, trichloroisobutylsilane, trichlorophenylsilane, trichlorooctylsilane, and trichlorododecylsilane (see Appendix A for structures) were used as grafting agents. In a Schlenk tube, 0.1-0.5 g dried SBA-15 was combined with 10 mL toluene. The alkylsilane grafting agent was added slowly in 2 – 10× excess. The solution was refluxed at 110°C for 20 hours. The alkylsilane-grafted SBA-15 was dried under vacuum at 80°C for 15 hours. To eliminate the presence of residual hydrochloric acid (HCl) formed during grafting, some samples of grafted SBA-15 using chlorosilanes were washed with water before being dried at conditions stated above. Figure 4 depicts the chemistry for the grafting reactions of silanes on SBA-15. The grafting of alkoxy silanes on mesoporous silica results in the formation of the corresponding alkanol.

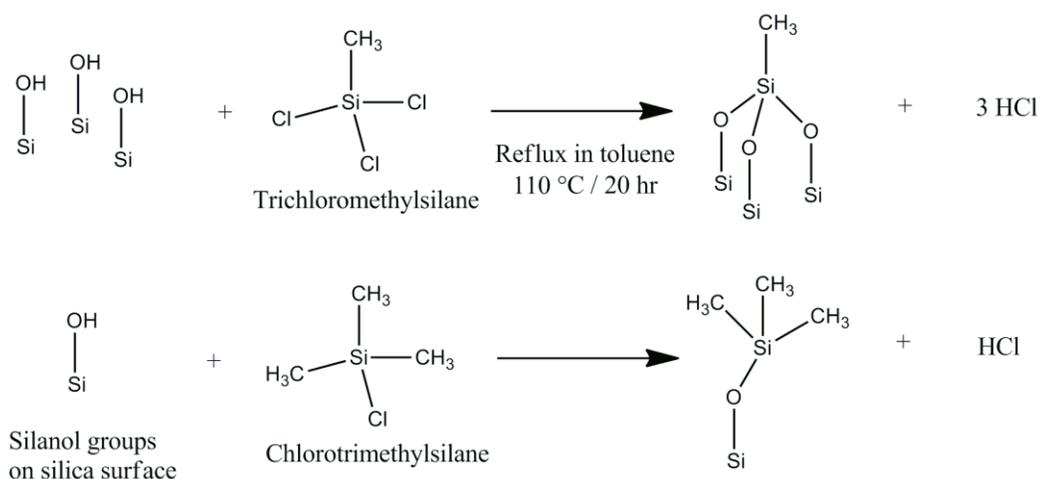


Figure 4. Scheme for grafting of silanes onto mesoporous silica surface.

The heat of wetting (ΔH_w) of dried, ungrafted SBA-15 and three polyhedral oligomeric silsesquioxanes (POSS) – octamethyl-POSS, octaisobutyl-POSS, and octaphenyl-POSS (see Appendix B for structures) – in water or dioxane were measured by solution calorimetry (Thermal Activity Monitor III, TAM III, TA Instruments Inc.) at $25 \pm 10^{-4} \text{ } ^\circ\text{C}$. Five to twenty mg of the powder was loaded into a glass ampoule. The ampoule was sealed with a rubber stopper and covered with melted wax. The ampoule was inserted into calorimeter arm, then into a 25 mL reaction vessel filled with the appropriate solvent. The ampoule was stirred at a constant rate of 600 rpm throughout experiment. The TAM III measured the heat released upon breaking of the ampoule. Figure 5 shows the TAM III and typical thermodynamic profile.

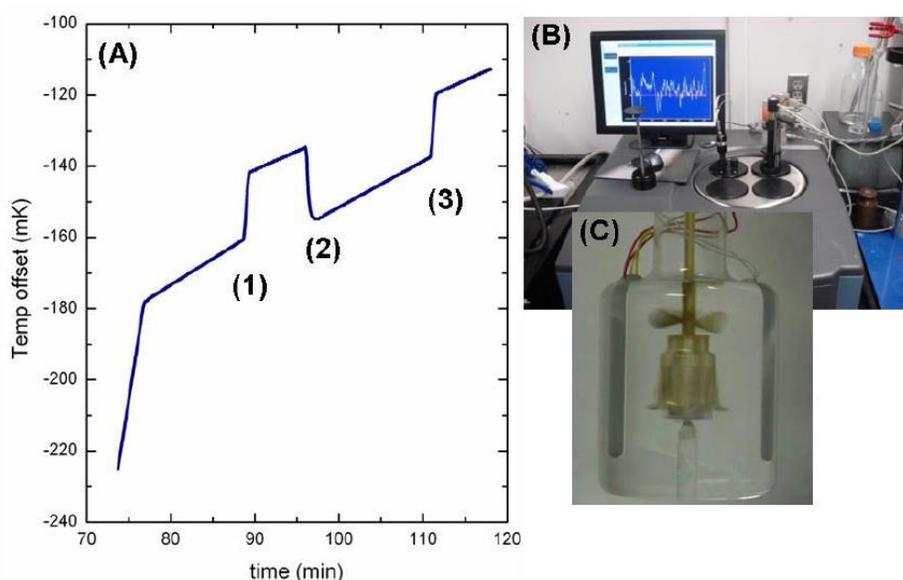


Figure 5. (A) Heat of solution experimental thermal profile for propanesulfonic acid. (B) TAM III Precision Calorimeter. (C) 25mL ampoule cell for solution calorimeter.

The heat of solution (ΔH_{soln}) of sulfuric acid and seven different sulfonic acids – methanesulfonic acid (MeSA), ethanesulfonic acid (EtSA), trifluoromethanesulfonic acid (MeF₃SA), tetrafluoroethanesulfonic acid (EtF₄SA), nonafluorobutanesulfonic acid (BuF₉SA), ethylbenzenesulfonic acid (EtBzSA), and benzenesulfonic acid monohydrate (BzSA•H₂O) (see Appendix C for structures) – in water or dioxane were measured by solution calorimetry (Thermal Activity Monitor III, TAM III, TA Instruments Inc.) at 25 ± 10^{-4} °C. Ten to thirty mg of appropriate acid sample was loaded into a glass ampoule. Solution calorimetry measurements were made using the same method and equipment as for the heat of wetting measurements.

Contact angle measurements on bare and silane-grafted SBA-15 were made using a Arame-Hart model 250 standard goniometer. The H₂O droplet was a 10 μ L volume.

Chapter 3

Results and Discussion

Solution calorimetry was used to measure the ΔH_w of pristine SBA-15 and selected silsesquioxanes in water and dioxane; these values are reported in Table 1.

Table 1. Heats of wetting of SBA-15 and silsesquioxanes.

Sample	ΔH_{water} [J/g] ^a	$\Delta H_{\text{dioxane}}$ [J/g] ^b
SBA-15	-101.7 ± 7.3	-131.6, -88.4
Octamethyl-POSS	32.5, -8.0	15.6
Octaisobutyl-POSS	15.4, 5.9 ^c , 6.9 ^c	73.7
Octaphenyl-POSS	34.1, -4.4, -9.9 ^c	15.4

^a In H₂O; ^b in dioxane; ^c well-ground sample

Silsesquioxanes are extremely hydrophobic organosilicon molecules with cage-like structures (see Appendix B for structures). Comparison of their ΔH_w values with those of SBA-15 in water pre- and post-grafting will help to assess the hydrophobicity of the grafted products because the POSS side chains are analogous to some of the homogeneous sulfonic acid backbones. From Table 1 it is shown that the ΔH_w of bare SBA-15 is very exothermic in both water and dioxane and the ΔH_w of most of the POSS samples are endothermic in both water and dioxane. This indicates that SBA-15 is strongly solvated and the POSS samples are weakly solvated in both solvents. POSS samples were extremely hydrophobic and the powder did not disperse itself in water. The insoluble POSS samples and modified SBA-15 samples do not suspend in the solution due to their extreme hydrophobic nature and thus their solution calorimetry measurements are reported as heats of wetting, ΔH_w . The POSS samples clung to the inside of ampoule and onto the calorimeter arm. In an attempt to better disperse the POSS

powder in water, some of the samples were ground with a mortar and pestle before they were loaded into the ampoule. This was done to eliminate aggregation of the material. Table 1 demonstrates this physical grinding decreased the ΔH_w of the samples. The POSS samples were almost completely suspended in the dioxane medium, a reflection of their organic nature. Only small amounts of each powder clung to the inside of the ampoule and remained undissolved. Due to the large variability in the ΔH_w measurements of the POSS samples, more data should be collected before conclusive comparisons are stated based on these results.

Table 2. Grafting information and heats of wetting for modified SBA-15.

Sample	Precursor	Reagent to –OH Ratio ^d	ΔH_{water} [J/g]
CH₃-grafted <i>(washed)</i> ^c	-Cl	3×	-35.1, -37.9
	-Cl	3×	-58.6
tri-CH₃-grafted	-Cl	3×	-38.2, -38.1
Isobutyl-grafted <i>(washed)</i>	-Cl	3×	-74.0, -65.1
	-Cl	3×	-23.5, -72.6
Phenyl-grafted <i>(washed)</i>	-OEt	10×	-63.8, -60.6
	-Cl	10×	-125.2, -112.3
	-Cl	10×	-61.7, -52.1
Octyl-grafted <i>(washed)</i>	-OEt	10×	-73.1, -69.3
	-Cl	10×	-127.8, -108.9, -117.7
	-Cl	10×	-22.6
Dodecyl-grafted <i>(washed)</i> <i>(washed)</i>	-Cl	10×	-51.0, -44.3, -56.0, -59.9
	-Cl	10×	-8.8, -13.5
	-Cl	3×	-32.5
Octadecyl-grafted	-OMe	2×	-64.0, -58.2
	-OMe	6×	-42.4

^d Indicates in how much excess (of –OH group surface density) silane reagent was present during grafting; ^csample washed with water to remove residual acid

The ΔH_w for all grafted SBA-15 solutions is shown in Table 2. Precursors are defined by whether they were a methoxysilane, ethoxysilane, or a chlorosilane. The reagent to $-OH$ ratio details how much excess each reagent was used compared to the number of hydroxyl groups ($-OH/g$). In the case of chlorosilane precursors, it was expected these would yield better grafting results as the chloro group is more electronegative than an alkoxy group. Initially this did not seem to be true based on results of phenyl- and octyl- silane grafting. Another unexpected result was that the phenyl- and octyl- grafted silanes using chloro precursors had more negative heats of wetting (-118.8 and -118.1 J/g respectively) than that of bare SBA-15 (-101.7 J/g). This seems to indicate that post-grafting, these samples were less hydrophobic than they were before grafting. This is completely inconsistent with previous observations that the grafting of alkyl and aryl fragments to SBA-15 led to a significant decrease in the heat of wetting of silica. It was hypothesized that the increased exothermicity of the wetting experiment was due to residual hydrochloric acid left on the sample post-grafting. Hydrochloric acid dissolves very exothermically in water, so this would explain the decreased value in the heat of wetting. This hydrochloric acid would be the result of the chloro group from the silane agent and the hydrogen removed from the surface hydroxyl groups during grafting. To confirm this theory, the chlorosilane grafted silicas were washed with water and the pH of the effluent water was measured. The results indicated the water samples were very acidic, confirming the presence of acid in the grafted samples. To remove this acid, all samples grafted using chlorosilane precursors were washed with water until the effluent water registered a neutral pH. The washed samples were then dried at $80^\circ C$ for 15 hours and their ΔH_w were measured again. The differences between washed and unwashed chlorosilane grafted samples are shown in Figure 6. After washing the ΔH_w of all samples except the CH_3 - grafted sample increased (became more positive). Since the ΔH_w of the CH_3 - grafted sample was only tested once after washing, it is assumed that this number may be an experimental error. For this reason, the pre-washed value

will be taken as the correct ΔH_w in this particular case. A comparison of the ΔH_w for washed chlorosilane versus alkoxy silane grafting in the cases of phenyl- and octyl- grafted samples shows the anticipated result of chlorosilane grafting yielding a less negative value. For phenyl-grafted SBA-15, the alkoxy silane grafted value is -62.2 J/g, while the chlorosilane grafted value is -56.9 J/g. Similarly, for octyl-grafted SBA-15, the alkoxy silane grafted value is -71.2 J/g, while the chlorosilane grafted value is -22.6 J/g. These results indicate the chlorosilane precursors provide better grafting results than alkoxy silane grafting precursors because they yield less negative ΔH_w values due to less solvation of the surface of the SBA-15 support.

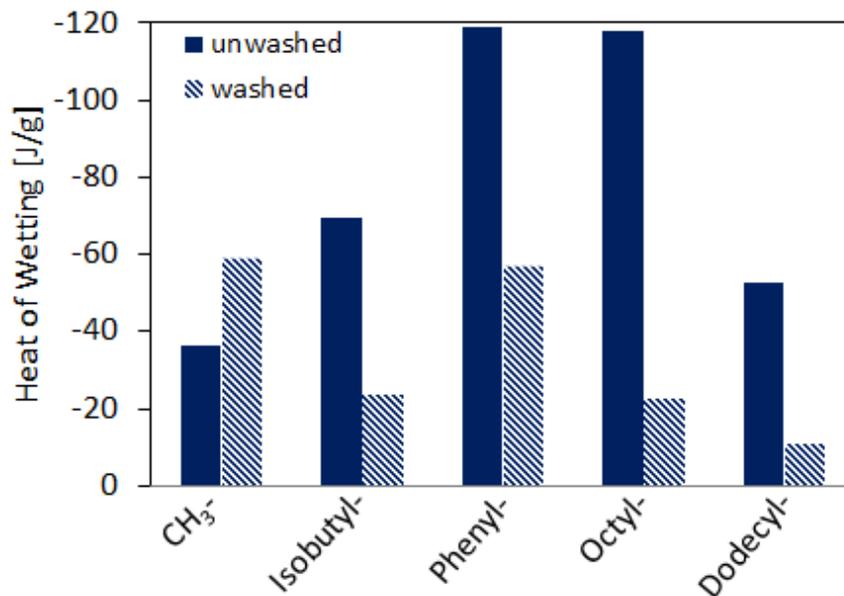


Figure 6. Comparison of heats of wetting for washed and unwashed modified SBA-15 using chlorosilane precursors.

Throughout this study, the grafting agents were used in varying amounts of excess. The necessary amount of silane grafting reagent excess is important to determining the best procedure for introducing hydrophobicity by grafting organic moieties onto SBA-15. Comparisons were done for both alkoxy silane and chlorosilane precursors. For the alkoxy silane precursors, the amount of trimethoxyoctadecylsilane was varied. When the silane grafting reagent was used in 2× excess of the surface hydroxyl groups, the ΔH_w was -61.1 J/g. When the silane grafting

reagent was in 6× excess, the ΔH_w was -42.4 J/g. For the chlorosilane precursors, the effects of varying the amount of trichlorododecylsilane were observed. At 3× excess, the ΔH_w of the dodecyl grafted SBA-15 was -32.5 J/g. When the reagent was present in 10× excess, the ΔH_w of the dodecyl grafted SBA-15 was -11.2 J/g. This study did not investigate the effect the silane grafting reagent would have if it were present in greater than 10× excess. In both the alkoxysilane and chlorosilane cases, the ΔH_w was found to be less negative in the cases where a greater amount of excess grafting reagent was used as compared to lesser amount of excess reagent. This indicates more effective grafting is achieved when grafting reagents are used in a large amount of excess. More effective grafting also indicates the sample has been made more hydrophobic and less solvation of the surface of the SBA-15 support has occurred. Less solvation of the silica support is the desired outcome, as this indicates less solvation of the active site of a heterogeneous catalyst would occur if surrounded by these types of hydrophobic modifications on a mesoporous silica support.

The objective of this study is to make hydrophobic modifications to SBA-15 silica and determine to what degree the modification changes the measured hydrophobicity of SBA-15 silica. Figure 7 compares the ΔH_w of all of the modified SBA-15 samples. It is important to note that the lowest ΔH_w average for each silane grafting agent was used. In most cases this was the sample that used the largest excess of silane reagent to hydroxyl group density during grafting. For silane reagents that were not available with a chloro precursor, the alkoxy precursor value is shown. All modified SBA-15 samples show a more positive ΔH_w than the bare, unmodified SBA-15. The expected trend would be that the ΔH_w should become increasingly more positive with increasing organic moiety size due to the anticipated outer-sphere effects. This is not necessarily reflected in the results. In particular, it would be expected that the values for the triCH₃-, phenyl-, and octadecyl-modified SBA-15 samples would have lower ΔH_w than were actually observed in this study. One possible explanation for their more negative than expected

values is the fact that all of the organic moieties of these silane grafting agents are bulky molecules. It is possible that due to their size, they inhibited grafting of more like molecules on the hydroxyl groups next to them. This would mean that water was able to solvate more of the modified SBA-15 surface due to available hydroxyl groups. Consequently, this could lead to a more negative ΔH_w than was anticipated. Water is a much smaller molecule than the silane grafting reagents and could access the available hydroxyl groups more easily. Surface area measurements would be able to confirm this occurrence. Another possible explanation, particularly in the cases of triCH₃- and octadecyl- modified SBA-15, is less than ideal grafting conditions. Neither silane reagent was used in 10× excess as was the case with most other grafting trials. Trimethoxyoctadecylsilane is also not available in an analogous chlorosilane precursor, which is believed to be more effective for grafting octadecyl groups to SBA-15. Further grafting experiments should be conducted to confirm the best method for modifying SBA-15 and these should be applied to all silane precursors. From the available data from this study, dodecyl-grafted SBA-15 shows the most positive ΔH_w and therefore is indicative of the most successful hydrophobic modification of SBA-15.

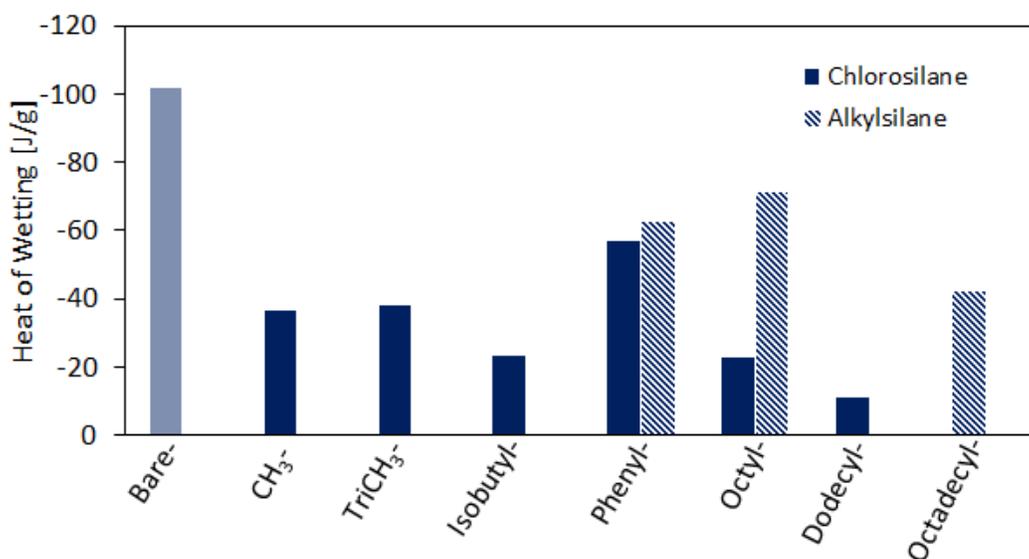


Figure 7. Heats of wetting for all modified SBA-15 samples.

Contact angle measurement data was taken for grafted samples and bare SBA-15. Water was absorbed nearly immediately onto the surface of bare SBA-15 and most other grafted samples. Absorption occurred too quickly for a contact angle to be established. The only sample for which a contact angle was able to be established was dodecyl-grafted SBA-15. This is further evidence of the hydrophobicity of dodecyl-grafted SBA-15. The established contact angle for dodecyl-grafted SBA-15 was 120.8°. Figure 8 shows the comparison between the absorption of water to bare SBA-15 and the contact angle of water on dodecyl-grafted SBA-15.

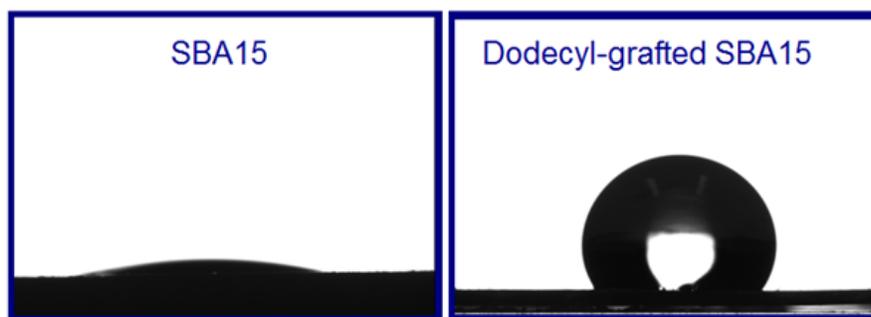


Figure 8. Contact angle measurements for bare SBA-15 and dodecyl-grafted SBA-15.

The ΔH_w of CH₃-, isobutyl-, and phenyl-modified SBA-15 samples can be compared to those of the corresponding POSS structures that were reported in Table 1. Due to their similar structures, it is expected that their results would yield similar values. The ΔH_w values reported for POSS structures are, in fact, much less negative than the modified SBA-15 structures. This indicates that not all of the hydroxyl functional groups on the SBA-15 surface have been modified with organic moieties. In order to quantify the amount of modification coverage on SBA-15, surface area measurements would be required.

Table 3. Heats of solution in H₂O and dioxane and pKa values for sulfuric acid and various sulfonic acids.

Acid	pKa	ΔH_{water} [J/g]	$\Delta H_{\text{dioxane}}$ [J/g]
H ₂ SO ₄	-3.0	-69.7 ± 1.1	-25.6 ± 0.0
CH ₃ SO ₃ H (MeSA)	-1.92	-46.0 ± 2.4	-10.8 ± 0.0
C ₂ H ₅ SO ₃ H (EtSA)	-1.68	-45.7 ± 1.5	-8.5 ± 0.0
CF ₃ SO ₃ H (MeF ₃ SA)	-5.2 ± 1.3	-67.1 ± 2.2	-53.4 ± 0.0
CHF ₂ CF ₂ SO ₃ H (EtF ₄ SA)	-3.5 ± 0.5 ^f	-73.4 ± 2.8	-46.0 ± 0.0
C ₄ F ₉ SO ₃ H (BuF ₉ SA)	-3.5 ± 0.5 ^f	-71.7 ± 1.9	-39.7 ± 0.0
C ₂ H ₅ C ₆ H ₄ SO ₃ H (EtBzSA)	-1.8 ± 0.5 ^f	-39.5 ± 1.1	-7.7 ± 0.0
C ₆ H ₅ SO ₃ H•H ₂ O (BzSA•H ₂ O)	-2.8 ^g	-9.4 ± 0.0 ^g	23.9 ± 0.0 ^g

^fEstimated based on equation found in Guthrie¹⁰, using σ value¹¹; ^gpKa value for anhydrous form

The heats of solution, ΔH_{soln} , of the sulfonic acids observed in this study are reported in Table 3. The only sulfonic acids that were more strongly solvated by water than sulfuric acid were those containing fluorine groups, EtF₄SA and BuF₉SA. MeF₃SA was also very strongly solvated by water and had a ΔH_{soln} near that of sulfuric acid. Those that do not contain fluorine have ΔH_{soln} that become more positive with increasing length of the organic moiety. It is important to note that BzSA was only used in its monohydrate form in this study and for a more accurate description of this trend, BzSA•H₂O would need to either be corrected for the heat of fusion or the solution calorimetry measurements would need to be repeated with the anhydrous form. The overall trend indicates a larger organic moiety leads to decreased solvation of the acid moiety, or what would be the active site of the sulfonic acid catalyst.

Figure 9 represents the relationship between the ΔH_{soln} in water and dioxane and pKa. BzSA•H₂O was excluded from this plot because its pKa value could only be obtained for the anhydrous form. The plot shows the positive correlation between pKa and ΔH_{soln} . The plot also

shows that the order of the ΔH_{soln} , for the acids, with the exceptions of MeF_3SA , remains the same for both solvents. This indicates that the extent of solvation is dependent upon the organic moiety structure.

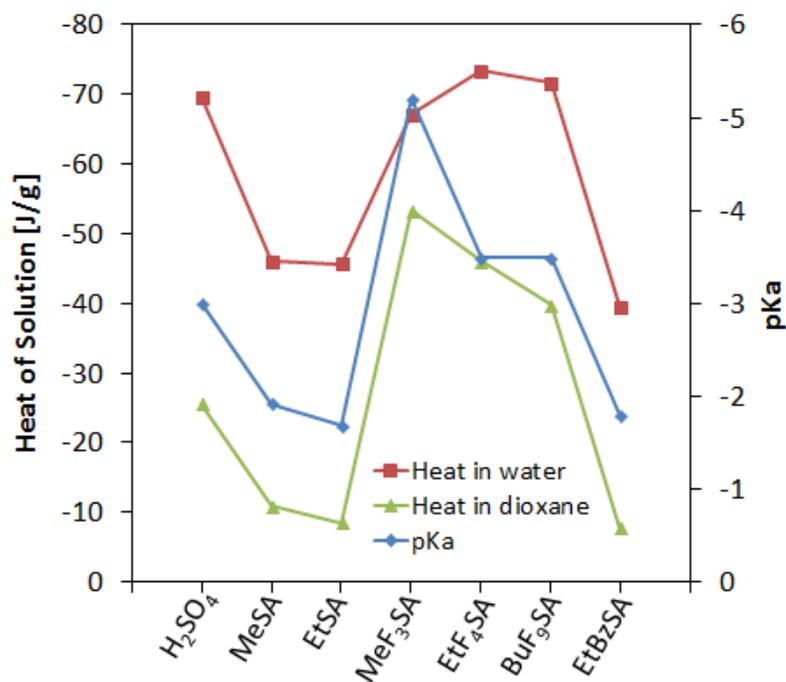


Figure 9. Heats of solution in water and dioxane compared with sulfonic acid pKa. Note: BzSA monohydrate was not included in this plot.

Chapter 4

Conclusion

Heterogeneous sulfonic acid catalysts show promise for use in the upgrading of bio-oil. Solution calorimetry results have shown that significant outer-sphere hydrophobic modifications can be made to the SBA-15 mesoporous silica support to reduce water solvation. Solution thermodynamics have also showed the degree to which inner-sphere modifications of sulfonic acids influence solvation. Both inner- and outer- sphere hydrophobic effects show a general trend of increasing hydrophobicity of the overall molecule with increasing hydrophobicity of the organic moiety. It is anticipated that this trend of increasing hydrophobicity will also be observed in heterogeneous sulfonic acid catalysts with hydrophobic inner- and outer-sphere modifications as the hydrophobicity of the organic moiety is increased, but more data is needed for conclusive results. The results of this study and best determined methods for grafting silanes on SBA-15 can serve as a basis for and be reapplied to other catalytic designs where water tolerance is a necessity for catalytic function and performance.

Chapter 5

Further Research

Solution thermodynamic measurements for sulfonic acids and silane-grafted SBA-15 were only repeated a few times each. Further measurements would help to better define the uncertainties associated with these results. Further research on the effectiveness of alkoxy- versus chloro- silane grafting reagents and the silane reagent to SBA-15 hydroxyl group density ratio will help to define the best procedure for grafting of silane agents on mesoporous silica. In addition, further research should be done to quantify the surface area of mesoporous silica after silane modification as well as on the proper procedure for the synthesis of heterogeneous sulfonic acid catalysts with outer-sphere hydrophobic modifications and on the solution thermodynamics of these catalysts. Finally, kinetic rate data for catalytic activity and conversion will need to be collected for these modified heterogeneous catalysts in order to determine their applicability for bio-oil upgrading. This additional research will lead to a better understanding of hydrophobic modified heterogeneous catalysts for use in water intolerant systems.

Appendix A

Relevant Silane Grafting Agent Structures

Alkoxysilanes

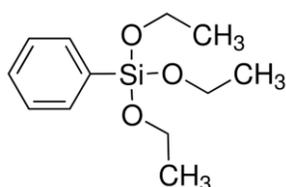


Figure 10. Structure of Triethoxyphenylsilane

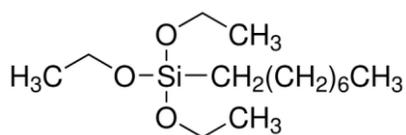


Figure 11. Structure of Triethoxyoctylsilane

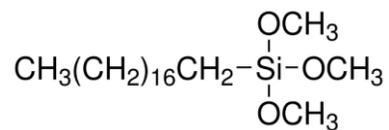


Figure 12. Structure of Triethoxyoctadecylsilane

Chlorosilanes

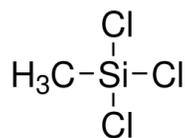


Figure 13. Structure of Trichloromethylsilane

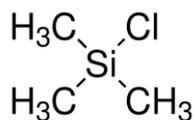


Figure 14. Structure of Trimethylchlorosilane

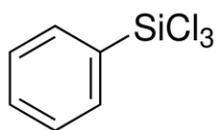


Figure 15. Structure of Trichlorophenylsilane

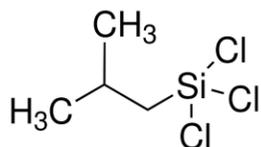


Figure 16. Structure of Trichloroisobutylsilane

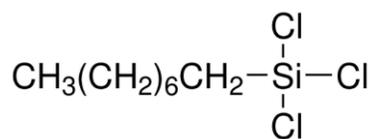


Figure 17. Structure of Trichlorooctylsilane

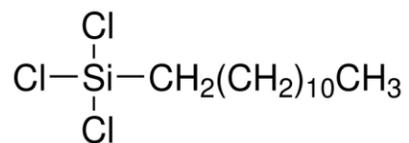


Figure 18. Structure of Trichlorododecylsilane

Appendix B

Relevant Silsesquioxane (POSS) Structures

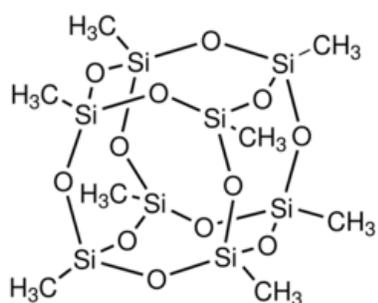


Figure 19. Structure of Octamethyl-POSS

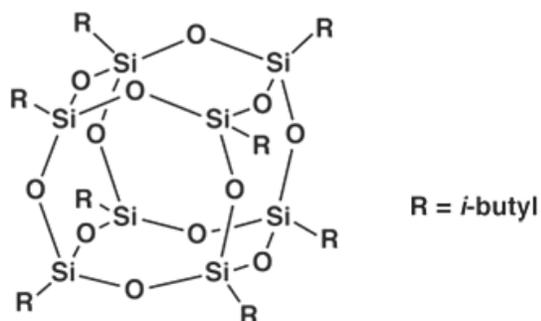


Figure 20. Structure of Octaisobutyl-POSS

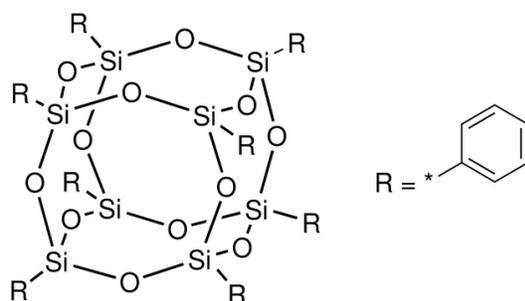


Figure 21. Structure of Octaphenyl-POSS

Appendix C
Relevant Sulfonic Acid Structures

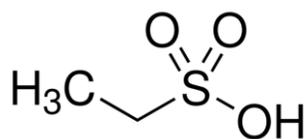


Figure 22. Structure of Methanesulfonic acid

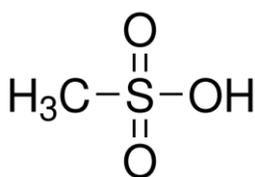


Figure 23. Structure of Ethanesulfonic acid

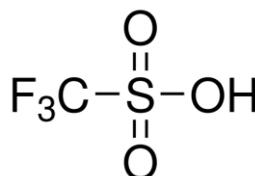


Figure 24. Structure of Trifluoromethanesulfonic acid

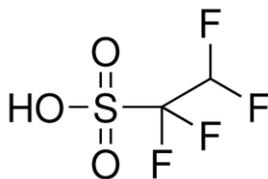


Figure 25. Structure of Tetrafluoroethanesulfonic acid

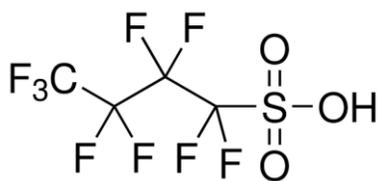


Figure 26. Structure of Nonafluorobutanesulfonic acid

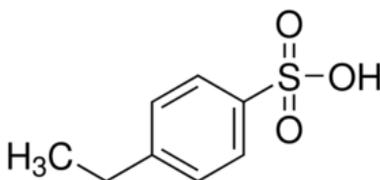


Figure 27. Structure of Ethylbenzenesulfonic acid

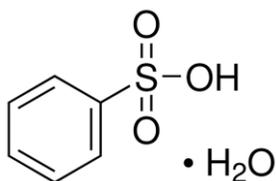


Figure 28. Structure of Benzenesulfonic acid monohydrate

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